

## PATENT ABSTRACTS OF JAPAN

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(54) ACRYLIC SOL

(57)Abstract:

PURPOSE: To obtain an acrylic sol which does not, unlike a polyvinyl chloride sol, generate hydrogen chloride even when incinerated, has a good storage stability, and gives a coating film hardly allowing a plasticizer to bleed out by compounding fine acrylic polymer particles each having a specific structure, a specific plasticizer, and a filler as the main components.

CONSTITUTION: An acrylic sol contains, as the main components, fine acrylic polymer particles each having a multilayered, at least bilayered, structure comprising a core and a shell, a dialkyl phthalate plasticizer, and a filler. Pref. the wt. ratio of the core to the shell of the particle is (25:75)-(70:30).

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CLAIMS

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[Claim(s)]

[Claim 1] Acrylic polymer particle (A) Plasticizer (B) And bulking agent (C) It is the acrylic sol constituent used as a principal component, and is this acrylic polymer particle (A). It consists of particles of the polymer which consists of the core section and the shell section and which has the double layer structure more than two-layer at least, and is this plasticizer (B). Acrylic sol characterized by being a dialkyl phthalate system plasticizer.

[Claim 2] acrylic polymer particle (A) \*\*\*\*\* -- acrylic sol according to claim 1 to which the polymer ratio of the core section and shell section is characterized by being a core / shell =25 / 75 - 70/30 (% of the weight).

[Claim 3] Acrylic polymer particle (A) It carries out. The polymer presentation of the core section Ethyl methacrylate, Normal butyl methacrylate, isobutyl methacrylate, tertiarybutyl methacrylate, Are chosen out of cyclohexyl methacrylate and ethylhexyl methacrylate. It consists of polymers which contain a kind of monomer unit 50% of the weight or more at least. Claim 1 characterized by being the polymer which contains a kind of monomer [ at least ] unit as which the polymer presentation of the shell section is chosen from methyl methacrylate, benzyl methacrylate, and styrene 50% of the weight or more, or an acrylic sol according to claim 2.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Industrial Application]** This invention relates to the acrylic plastisol which consists of an acrylic polymer particle, a plasticizer, and a bulking agent, and the acrylic organosol which added the organic solvent to this acrylic plastisol.

**[0002]**

**[Description of the Prior Art]** The plastisol constituent called current and the paste resin used widely industrially is a vinyl chloride sol which a plasticizer is made to distribute polyvinyl chloride powder and a bulking agent, and is obtained, and what added the pigment, the thermostabilizer, the foaming agent, the diluent, etc. further by the application is used. This vinyl chloride sol is used in many fields by the various purpose as a coating material for the object for automobiles, the object for carpets, the object for wallpaper, and floors etc.

**[0003]** On the other hand, by the latest global environment problems, this vinyl chloride sol serves as a basis of the destructive causative agent of an ozone layer in order to generate hydrogen chloride gas at the time of that incineration, and it has further the trouble of it not only becoming the cause of acid rain, but damaging an incinerator remarkably at the time of incineration of the product using a vinyl chloride sol, and waits for the appearance of the plastisol constituent replaced with the vinyl chloride sol which does not have such a difficulty in each goods field.

**[0004]** In JP,55-16177,B, (1) t-butyl acrylate, the alkyl methacrylate of C1-C4 Or a kind of a kind of cyclohexyl methacrylate, more than it, or the (2) above-mentioned monomer, or more than it And C2-C10 The methacrylate of fatty alcohol, and C1-C10 Acrylate of fatty alcohol, With the polymer which consisted of units guided from a kind of the comonomer chosen from styrene and alpha methyl styrene, or more than it The glass transition temperature of 35 degrees C or more, and 400 It has large average degree of polymerization, and is mean particle diameter 0.1-500. Organic polymer component 100 which is mum Weight section, It is 700 by the plasticizer 30 - the 1000 weight sections, and request. Invention about the plastisol which consists of an inert filler to the weight section and an additive usually used is indicated. The publication of the purport which can also copolymerize the acrylic monomer and/or methacrylic monomer which had the isolation carboxyl group, the hydroxyl, epoxy group, or amino group to about 3 % of the weight in the organic polymer component used here for the adhesive improvement to the base material of the paint film formed from the plastisol is made.

**[0005]** In order to form the paint film equipped with the good engine performance, as a plasticizer, dioctyl phthalate, dinonyl phthalate, JIDESHIRU phthalate, butyl cyclohexyl phthalate, etc. are mentioned to said official report. However, dioctyl phthalate etc. is cheap and it is shown in the 1st table that said acrylic sol which used the dialkyl phthalate system plasticizer which can be used advantageously industrially does not turn into a plastisol which thickening nature is very high and can be equal to practical use.

**[0006]**

**[Problem(s) to be Solved by the Invention]** The dissolution by the plasticizer of an acrylic polymer

particle is quick, when the high plasticizer of the plastic effectiveness like dialkyl phthalate system plasticizers, such as dioctyl phthalate and JISO nonyl phthalate, is used using the granular polymer of a homogeneity presentation system, a viscosity rise of an acrylic sol breaks out in several minutes after mixing with an acrylic polymer particle and a plasticizer, and it becomes impossible [ coating ], can be practically used as an acrylic sol, and is, and the acrylic sol shown in JP,55-16177,B is \*\*.

[0007] Moreover, although that coating nature and storage stability of the acrylic sol which mixed and made the polymer particle and dialkyl phthalate which made the solubility to a plasticizer small for the polymer presentation improve, since the compatibility of a polymer and a plasticizer is small, a plasticizer carries out bleed out of the paint film formed from this acrylic sol to a paint film front face with the passage of time after membrane formation, and a practical paint film is not obtained.

[0008] That is, although hydrogen chloride gas is not generated in the acrylic sol developed conventionally at the time of the incineration of a product which used it, the present condition is that the acrylic sol equipped with the practicality ability which can form the paint film which thickens also in the storage during the number day of \*\*s by hypoviscosity, and does not have the BURITO out of a plasticizer is not obtained.

[0009]

[Means for Solving the Problem] Then, this invention person etc. does not have generating of a hydrogen chloride like a vinyl chloride sol at the time of the incineration. The result wholeheartedly examined for the purpose of the thing which were mentioned above even if it used dialkyl phthalate system plasticizers, such as dioctyl phthalate and JISO nonyl phthalate, and for which it solves and the inconvenient acrylic sol which is not is developed, By [ which consist the acrylic polymer particle to be used of the core section and the shell section ] considering as the double layer structure more than two-layer at least, it found out that the above-mentioned technical problem was solvable. That is, the place made into the summary of this invention is an acrylic polymer particle (A). Plasticizer (B) And bulking agent (C) It is the acrylic sol constituent used as a principal component, and is an acrylic polymer particle (A). It is the particle of the polymer which consists of the core section and the shell section and which has the double layer structure more than two-layer at least, and is a plasticizer (B). It is in the acrylic sol characterized by being a dialkyl phthalate system plasticizer.

[0010] Acrylic polymer particle used for this invention (A) Although it will not be limited especially if a particulate structure can form the double layer structure more than two-layer at least, the core section is good to constitute from a plasticizer compatibility polymer and to constitute the shell section from a plasticizer non-compatibility polymer, and what is depended on the emulsion polymerization which can obtain especially a particle-like polymer efficiently is good. Acrylic polymer particle (A) The polymer ratio of the core section and the shell section is good to be referred to as a core / shell =25 / 75 - 70/30 (% of the weight).

[0011] Acrylic polymer particle (A) The purpose which makes a particulate structure a core/shell structure carries out coating of this acrylic sol, and is in the point of protecting the bleed out of a plasticizer from the paint film after heating and membrane formation while it aims at improvement in the storage stability of the acrylic sol made using this polymer particle.

[0012] Although it is dependent also on the comonomer component which constitutes the core section and the shell section, when a plasticizer and a polymer with the highest compatibility are used for the core section, an acrylic sol with the polymer ratio of the core section and the shell section sufficient [ balance with 25/75 (% of the weight) of acrylic polymers ] is obtained. The bleed out of a plasticizer generates the paint film formed from the acrylic sol obtained using the acrylic polymer particle with few core components than this. Moreover, when a plasticizer and a polymer with the lowest compatibility are used for the shell section, the good acrylic sol of balance is obtained for the polymer ratio of the core section and the shell section with the acrylic polymer of a core / shell =70 / 30 (% of the weight). By the acrylic polymer particle with few shell components, covering to the core section of a shell component becomes poor from this, in the acrylic sol obtained using the acrylic polymer particle of such structure, a viscosity rise of an acrylic sol becomes quick by the dissolution of the acrylic polymer particle by the plasticizer, and the storage stability runs short.

[0013] Acrylic polymer particle (A) It is desirable to constitute at least a kind of methacrylate chosen from ethyl methacrylate, normal butyl methacrylate, isobutyl methacrylate, tertiarybutyl methacrylate, and cyclohexyl methacrylate or those copolymers from a polymer contained 50% of the weight or more as a component of the core section.

[0014] Thus, as for the core component of this invention, what has high compatibility with a dialkyl phthalate system plasticizer is desirable, and since the bleed out of a plasticizer does not occur after membrane formation, the paint film formed from the acrylic sol containing the acrylic polymer particle to which the amount of copolymerization of the above-mentioned monomer uses 50% or more of copolymer as a core is desirable.

[0015] As a monomer which can copolymerize other, it is C1-C13. Acrylate of alcohol (meta), Acrylic nitril, acrylamide, methacrylamide, N-dimethyl acrylamide, N-dimethyl methacrylamide, N-dimethylaminoethyl methacrylate, N-diethylamino ethyl methacrylate, acrylonitrile, vinyl acetate, Styrene, alpha methyl styrene, an acrylic acid, a methacrylic acid, a crotonic acid, An itaconic acid, hydroxyethyl acrylate, hydroxypropyl acrylate, Hydroxyethyl methacrylate, hydroxypropyl methacrylate, ethylene glycol dimethacrylate, a divinylbenzene, glycidyl methacrylate, allyl compound methacrylate, etc. are mentioned, and it can be used in these kinds or two sorts or more of combination.

[0016] Moreover, acrylic polymer particle (A) It is desirable to copolymerize at least a kind of methacrylate chosen from methyl methacrylate, benzyl methacrylate, and styrene or those copolymers 50% of the weight or more as a component of the shell section. Acrylic polymer particle used by this invention (A) As for a shell component, what has low compatibility with a dialkyl phthalate system plasticizer is desirable, and that poor coating and poor storage stability occur by viscosity rise of the acrylic sol which the diffusion to the polymerization inside of the body of a plasticizer is checked, and is obtained using this polymer particle has very few acrylic polymer particles to which the amount of copolymerization of the above-mentioned monomer constituted shell from 50% or more of a polymer. As a copolymerization monomer of others which it faces making the polymer which constitutes shell and can be used C1-C13 Acrylate and methacrylate of alcohol, Acrylic nitril, acrylamide, methacrylamide, N-dimethyl acrylamide, N-dimethyl methacrylamide, N-dimethylaminoethyl methacrylate, N-diethylamino ethyl methacrylate, acrylonitrile, vinyl acetate, Styrene, alpha methyl styrene, an acrylic acid, a methacrylic acid, a crotonic acid, An itaconic acid, hydroxyethyl acrylate, hydroxypropyl acrylate, Hydroxyethyl methacrylate, hydroxypropyl methacrylate, ethylene glycol dimethacrylate, a divinylbenzene, glycidyl methacrylate, allyl compound methacrylate, etc. are mentioned, and it can be used in these kinds or two sorts or more of combination.

[0017] The molecular weight of the polymer of an acrylic polymer particle is 10,000-2,000,000 at weight average molecular weight, although it changes with applications of an acrylic sol. It is desirable. Beyond the room temperature of Tg of an acrylic polymer is desirable. The paint film formed from the acrylic sol which Tg made using the particle of the acrylic polymer below a room temperature does not become easy to be discovered and have desirable tuck nature.

[0018] The mean particle diameter of an acrylic polymer particle is 0.1-100. It is desirable to use the thing of the range of  $\mu\text{m}$ . Mean particle diameter Exceeding 100 micrometers, it becomes poor at the time of the heating membrane formation spreading [ of the plasticizer into an acrylic polymer particle ] the acrylic sol using a large acrylic polymer particle, and it becomes difficult to make perfect gelation of a paint film cause. Moreover, mean particle diameter The acrylic sol using an acrylic polymer particle smaller than 0.1 micrometers becomes insufficient [ the storage stability ].

[0019] The mean particle diameter of an acrylic polymer particle is doubled with the mode which applies an acrylic sol, and should just choose mean particle diameter.

[0020] The plasticizers used for this invention are dialkyl phthalate system plasticizers, such as dioctyl phthalate, IIISO nonyl phthalate, di-isodecyl phthalate, and di-undecyl phthalate. Especially, dioctyl phthalate and IIISO nonyl phthalate have a cheap price, and are industrially desirable. The mixed ratio of an acrylic polymer particle and a plasticizer is the acrylic polymer particle 100. They are plasticizers 50-500 per weight section. Using at a rate of the weight section is desirable.

[0021] The bulking agents used for this invention are a calcium carbonate, baryta, clay, colloidal silica,

mica powder, diatomite, a kaolin, talc, a bentonite, glass powder, sand, oxidization and an aluminum hydroxide, an antimony trioxide, a titanium dioxide, carbon black, metal soap, a color, a pigment, etc. Preferably, it is the acrylic polymer particle 100. Per [ 50-500 ] weight section It is good to use the bulking agent of the weight section.

[0022] Solvents above else, such as mineral turpentine, can be added to the acrylic sol of this invention as a diluent, and it can also consider as an organosol. Furthermore according to the purpose of using an acrylic sol, various kinds of additives, for example, an adhesion promoter, a leveling agent, a tack inhibitor, a release agent, a defoaming agent, a foaming agent, a surfactant, an ultraviolet ray absorbent, lubricant, a flame retarder, perfume, etc. can be blended.

[0023] As an approach of applying the acrylic sol of this invention to a base material, various approaches, such as a dipping process besides the paint film fabricating methods, such as coatings and DIP molding, such as DIP coating, knife coating, roll coating, and curtain flow coating, cast molding, slash molding, and low TESHONARU molding, brush coating, spray painting, and electrostatic coating, can be used.

[0024] In order to make the coating object created using the acrylic sol of this invention gel, suitable gel formation temperature and the gelation processing time are required. The range of 70 - 260 \*\* and the gelation processing time are [ gel formation temperature ] good to consider as the range for 30 seconds - 90 minutes. An acrylic sol can form the uniform film on this gelation condition.

[0025] The acrylic sol of this invention can be applied to a coating, ink, adhesives, a binder, a sealing agent, etc., and can be applied also to mold goods, such as miscellaneous goods, a toy, industrial components, and an electrical part. Moreover, if it applies to paper, cloth, etc., it will become artificial leather, matting, wallpaper, garments, a tarpaulin, etc., and if it applies to a metal plate, it can consider as an anti-corrosiveness metal plate.

[0026] An example is used for below and this invention is explained to it. The section in an example shows the weight section.

[0027]

[Example 1] The water 1967 section, the polyoxyethylene nonylphenyl ether (emulgen 910 by Kao Corp.) 12.5 section, and the potassium persulfate 0.75 section are supplied to 5l. 4 opening flask, and it is isobutyl methacrylate 250. The section was added, the heating polymerization was carried out at 70 degrees C among nitrogen-gas-atmosphere mind for 5 hours, stirring by 180rpm, and the core particle was formed according to the emulsion polymerization. Furthermore, it is methyl methacrylate 578. After adding the mixture of the section, the methacrylic-acid 6 section, and the dialkyl sulfo sodium-succinate (Pelex OTP by Kao Corp.) 8 section and performing a heating polymerization for 3 hours, the temperature up was carried out to 80 degrees C, it held for 1 hour, the shell component was formed according to the emulsion polymerization, and the emulsion containing the acrylic polymer particle of a core/shell mold was obtained. The minimum coat formation temperature (MFT) of the obtained emulsion was 103 \*\*, it was near the MFT of the methyl methacrylate polymer simple substance which constitutes the shell section, and since there was nothing at about 50 degrees C which is MFT of the isobutyl methacrylate polymer simple substance of the core section, or about 80 degrees C of a copolymerization polymer, it checked that the acrylic polymer particle contained in an emulsion was a polymer particle which has the two-layer structure of a core/shell. The obtained emulsion was fine-particles-sized using the spray dryer, and the acrylic polymer particle with a mean particle diameter of 10 micrometers was obtained. As a result of observing this acrylic polymer particle with an electron microscope, the primary particle 1 micrometer or less condensed, and it became clear that the spherical particle around 10 micrometers was formed. obtained acrylic polymer 100 the section -- JIISO nonyl phthalate 150 the viscosity [25 degrees C, E mold viscometer, and the Tokyo Keiki Co., Ltd. make] of the acrylic sol which added and obtained the section and the calcium-carbonate [neo [ made from Takehara Chemical industry ] light SP] 50 section -- 30,000cps it was . the viscosity (25 degrees C) after holding this sol for five days at 40 degrees C -- 40,000cps it was . This storage stability was enough practically. Moreover, when this acrylic sol was applied to the tin plate and it heated by 150 \*\* for 30 minutes, even if it formed uniform gel and held this paint plate for one week at 10 degrees C, there is no

bleed out of the plasticizer to a paint film side, and it confirmed that the compatibility of an acrylic polymer and a plasticizer was good.

[0028]

[Example 2] The acrylic polymer as Table 1 is obtained by the same technique as an example 1, except changing a plasticizer into dioctyl phthalate from JIISO nonyl phthalate, an acrylic sol is obtained like an example 1, the gelation film is made from this acrylic sol, and the result of having performed that evaluation is shown in Table 2.

[0029]

[An example 3, the examples 1-3 of a comparison] The acrylic polymer as Table 1 is obtained by the same technique as an example 1, an acrylic sol is made like an example 1, and the result of having evaluated the gelation film created from this acrylic sol is shown table 2.

[0030]

[The examples 5 and 6 of a comparison] The presentation with the core formation polymer and shell formation polymer which Table 1 shows by the same technique as an example 1 was made the same, the acrylic polymer particle without layer structure was obtained, the acrylic sol was made using this acrylic polymer particle, and the gelation film formed from this acrylic sol was evaluated. A result is shown in Table 2. In the example 5 of a comparison, the acrylic polymer dissolved in the plasticizer easily, acrylic sol viscosity rose, and it gelled two days after. Moreover, in the example 6 of a comparison, although viscosity change of an acrylic sol is small and that storage stability was good, from the acrylic polymer paint film which gelled the paint film formed from this acrylic sol like the example 1, the plasticizer dissociated, bleed out was carried out to the film front face, and that use was not completed.

[Table 1]

実施例	組 成 (wt %)		コア/シェル比 (wt %)
	コ ア 組 成	シ ェ ル 組 成	
実施例 1	iBMA = 100	MMA/MAA=99/1	30/70
実施例 2	iBMA/EMA/MAA=59/40/1	MMA/MAA=99/1	40/60
実施例 3	nBMA/CHMA=70/30	MMA/BzMA=60/40	60/40
比較例 1	iBMA = 100	MMA/MAA=99/1	20/80
比較例 2	iBMA = 100	MMA/MAA=99/1	75/25
比較例 3	iBMA/MMA/MAA=40/59/1	MMA/MAA=99/1	40/60
比較例 4	iBMA/MMA/MAA=70/29/1	MMA/EMA=45/55	40/60
比較例 5	iBMA/EMA/MAA=59/40/1	iBMA/EMA/MAA=59/40/1	——
比較例 6	MMA/BzMA=60/40	MMA/BzMA=60/40	——

注) iBMA : イソブチルメタクリレート

nBMA : ノルマルブチルメタクリレート

MMA : メチルメタクリレート

CHMA : シクロヘキシルメタクリレート

MAA : メタアクリル酸

BzMA : ベンジルメタクリレート

[Table 2]



実施例	ソル性能		塗膜性能	
	ソル粘度変化	貯蔵安定性	ブリードアウト	塗膜剥離
実施例1	○	○	○	○
実施例2	○～△	○～△	○	○
実施例3	○	○～△	○	○
比較例1	○	○	×	○
比較例2	×	×	○	○
比較例3	○	○	×	○
比較例4	×	×	○	○
比較例5	×	×	○	○
比較例6	○	○	×	×

## 〔ソル性能〕

ソル粘度変化 ; 40℃×6日間後の粘度／初期粘度

○ : < 2.0  
 △ : 2.0 ~ 3.0  
 × : > 3.0

貯蔵安定性 ; 40℃×6日間貯蔵後の塗工性

○ : 貯蔵前と変化はなく、塗工性は良好  
 △ : 3～4日目に増粘し、塗工性は少し低下  
 × : 貯蔵1日目にゲル化し、塗工不能

## 〔塗膜性能〕

ブリードアウト ; 成膜して10℃、1週間保持した後の塗膜面

○ : ブリードアウトなし  
 × : ブリードアウトあり

塗膜剥離 ; 成膜して10℃、1週間保持した後の塗膜面

○ : 塗膜剥離なし  
 × : 塗膜剥離あり

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